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Description

This invention relates to electrodes for use in electrochemical energy cells.

Bifunctional air electrodes for metal-air batteries, such as Iron-air batteries, generally consist of three components. These components are a hydrophobic layer which permits air passage while retaining electrolyte, and a dual component active layer attached thereto containing a catalytic active paste material, and a plurality of porous fiber metal current collectors in which the active paste is contained, as disclosed in U.S. Patent Specification No. 4,152,489, Chottiner et al.

The active paste material usually comprises an oxygen absorption/reduction carbon having a BET total surface area of from 30 to 1,500 square meters per gram, a suitable catalyst, an oxygen evolution metal additive, such as WS_2 or WC coated with 1 to 20 weight percent Co, and a dispersion of polytetrafluoroethylene as a bonding/nonwetting material, as disclosed in U.S. Patent Specification No. 4,152,489, Chottiner et al, and U.S. Patent Specification No. 3,977,901, Buzzelli. The active paste consists of the above admixture, mixed with deionized water, with no particular size or weight grading involved throughout the thickness of the active layer.

For good cell performance, the electrolyte must penetrate into the electrode sufficiently to reach the interior surface and contact air or other gas in the presence of catalyst. The electrode must at the same time be sufficiently electrolyte-repellent to prevent electrolyte flooding of the electrode pores. Electrolyte flooding has always been a problem with air electrodes, and while the Chottiner et al structure, and the Buzzelli active paste composition solved the problem to an acceptable degree, providing stable electrical characteristics for about 100 cycles, even more improved structures or compositions would be highly desirable, especially if electrolyte flooding could be completely eliminated.

An attempt to solve electrolyte flooding of gas electrodes in fuel cells by providing two zones in the electrode structure is disclosed in US Patent Specification No. 3423247, Darland Jr et al. One zone, next to the gas supply, consists of low surface area, large particles having high wetproofing and no catalyst, containing from 30 to 70 volume percent polytetrafluoroethylene. The other zone, next to the electrolyte, consists of high surface area, small, catalyzed particles operating in wetted condition. A single mesh current collector is attached to the zone next to the gas supply. Such a configuration is still not completely effective, however, and a need still exists for a maximum output, minimal flooding electrode for use in metal-air batteries and fuel cells.

Reference is made to Journal of Electrotechnical Society, Vol. 129, No. 6, June 1982, pages 1159 to 1164 by B G Demczyk et al, relating to an air electrode wherein the catalytically active layer comprises a catalyst and a mixture of hydrophobic and hydrophilic agglomerates.

Reference is also made to GB-A-1392353 disclosing an air electrode comprising a composite layer consisting of porous hydrophobic regions and catalytic hydrophilic regions, wherein the hydrophobic also hydrophilic regions interpenetrate one another.

The invention consists in an electrode for use in electrochemical energy cells which comprises: a porous backing sheet and a catalytically active layer comprising catalyst and a mixture of hydrophobic agglomerates and hydrophilic agglomerates, said layer being attached to said porous backing sheet having an electrolyte permeable side and a backing sheet contacting side, characterized in that the particle size of the hydrophobic agglomerates and the hydrophilic agglomerates increases from the electrolyte permeable side to the backing sheet contacting side and the weight ratio of hydrophobic material: hydrophilic material increases from the electrolyte permeable side to the backing sheet contacting side.

In one embodiment of the invention, the electrode is an air electrode in which the backing sheet is hydrophobic to which is laminated the catalytically active layer which has at least two porous metallic current collectors disposed therein, said hydrophobic agglomerates comprising oxygen absorption/reduction carbon particles having a total surface area of from 30 to 300 square meters per gram; catalyst, low oxygen overvoltage material, and fluorocarbon bonding/nonwetting material; and said active hydrophilic agglomerates comprising oxygen absorption/reduction carbon particles having a total surface area of from 30 to 300 square meters per gram, catalyst, low oxygen overvoltage material; fluorocarbon bonding/non-wetting material, and an organic dispersion agent effective to reduce liquid surface tension between the hydrophilic agglomerates; the weight ratio of active hydrophilic material: active hydrophobic material varying from 1:0.2 at the highly electrolyte permeable side to 1:5 at the hydrophobic sheet contacting side.

A suitable catalyst, such as silver, is preferably precipitate coated on the carbon particles.

Initially, all the active material is hydrophilic, but a portion of it is heat treated to thermally decompose the dispersion agent for the fluorocarbon, to provide a hydrophobic material which will retain electrolyte, because the dispersion agent is not present to reduce surface tension and allow good capillary flow of the electrolyte. The usual weight percent ratio of active hydrophilic material: active hydrophobic material in the active layer is from 40%:60%. The weight ratio of active hydrophilic material: active hydrophobic material through the thickness of the active layer of the electrode can range from 1:0.2 at the electrolyte contact surface to 1:5 at the air contact surface. By utilizing this configuration, catalyst is disposed throughout the active layer, the hydrophobic and hydrophilic regions are matched, and three phase interfacial contact of electrolyte, air and catalyst is maximized throughout the active layer thickness. It is to be understood throughout that the term "air" includes oxygen. In metal-air batteries, current is collected from all the

supporting metal current collectors simultaneously. Dramatically, stable electrical characteristics are achieved for up to about 300 cycles without electrode flooding or delamination due to trapped gases. Such electrodes are useful in a variety of metal-air batteries and fuel cells.

In order that the invention can be more clearly understood, a convenient embodiment thereof will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is an isometric view, in partial section, of one type of an air/metal battery, utilizing an electrode of the present invention;

Figure 2 is an enlarged sectional view of the electrode of Fig. 1 showing the particle size gradient of the hydrophilic and hydrophobic material through the active layer;

Figure 3 is a comparative graph showing oxygen reduction potential vs. cycle number; and

Figure 4 is a comparative graph showing oxygen evolution potential vs. cycle number.

Referring now to Fig. 1, the battery 10 shown in a general representation of metal/air cells of the present invention employing bifunctional air electrodes. Metal/air cell 10 includes a casing 11 for support of the air electrode and metal electrode as well as the electrolyte. Preferably, casing 11 is fabricated from ABS plastic or other non-conducting material that is stable or resistant to the electrolyte and reaction products, typically oxygen and hydrogen. Cell 10 comprises a pair of air electrodes 12 and 13 each having an outer hydrophobic sheet 14 and 16, respectively, each of which may be in contact with the atmosphere or other source of air or oxygen. Air electrodes 12 and 13 also include a plurality of active material sections 17 and 18, respectively, each active material section consisting of active material bonded to and contained in porous metallic plaques. These sections include integral metal current collectors 19 and 21. The plurality of active material sections make up the active layer. Electrodes 12 and 13 are framed in frames 22 and 23, preferably made from ABS plastic, and having electrical leads 24 and 26, respectively.

Metal/air cell 10 includes a metal electrode 27, fabricated from iron, cadmium, zinc or the like material, preferably iron, spaced between air electrodes 12 and 13 and including electrical lead 28. Metal/air cell 10 also includes an electrolyte 29 between and in contact with metal electrode 27 and air electrodes 12 and 13, respectively. Electrolyte 29 comprises an alkali hydroxide, preferably potassium hydroxide.

Fig. 2 shows in detail the electrode 12 of Fig. 1. As can be seen, the electrode is of a laminar construction. Cathode 12 is shown with a plurality of active material sections, making up the active layer 17, and a porous hydrophobic backing sheet 14 laminated thereto. Current collectors 19 used in metal-air battery applications are shown in the active layer 17 and are adapted for electrical connection to the circuit. In the preferred embodiment, at least two current collectors are used. The active material 30, comprises both hydrophilic agglomerates 31 and hydrophobic agglomerates 32 which coat, and bond to, and at least partially impregnate the current collectors 19, although such impregnation is not shown for sake of simplicity.

The current collector 19 can be made of expanded metal, such as nickel. It can also be made from expanded nickel coated iron or steel. Preferably it is made from nickel coated iron or steel fiber metal, or uncoated nickel, iron or steel fiber metal, for example, nickel or steel wool. Most preferably the metal fibers are diffusion bonded together and exceed 1.5 inches (3.81 cm) in length. Fiber diameters are usually from about 0.0002 inch (0.005 cm) to about 0.005 inch (0.127 mm). Diffusion bonding techniques are well known, and described in detail in U.S. Patent Specification No. 4,152,489. The current collector plaque 19 should have a porosity of from 75% to 95% and a thickness of between 0.005 inch (0.127 mm) and 0.050 inch (1.27 mm). For fuel cell electrode applications, current collectors can be excluded.

The active layer 17 is from 0.010 inch (0.254 mm) to 0.150 inch (3.81 mm) thick for metal-air battery applications and from 0.005 inch (0.127 mm) to 0.030 inch (0.762 mm) thick for fuel cell applications. The porous hydrophobic backing sheet 14 is from 0.005 inch (0.127 mm) to 0.020 inch (0.508 mm) thick for metal-air battery applications and from 0.002 inch (0.05 mm) to 0.020 inch (0.508 mm) thick for fuel cell application. The porous backing sheet 14 can comprise a porous pressed layer or sheet of particulate polytetrafluoroethylene or milled, fibrillated polytetrafluoroethylene fibers alone, or with either or a combination of unfibrillated fluorinated ethylene propylene fibers, carbon particles or fibers, polypropylene, polyethylene, and the like, as is well known in the art.

The plurality of active material sections constituting active layer 17, after their formation, for example, by individual cold pressing, which is particularly applicable for metal-air battery use, can be hot press or roll laminated together to form a consolidated laminar structure. The consolidated active layer 17 and the hydrophobic sheet 14 can then be press or roll laminated together at from 190°C to 350°C, with an air pressure of from 25 psi. to 750 psi (172 to 5165 kPa). Alternatively, the porous backing sheet can be attached during the active layer lamination process.

As can be seen from Fig. 2, the catalytically active material 30, constituting the active layer, comprises a mixture of both catalytically active hydrophobic and catalytically active hydrophilic material, both of whose agglomerates increase in particle size diameter from the electrolyte contact side 33 to the air contact side 34 of the electrode. Additionally, the weight percent of hydrophobic material in the active layer 17 increases from the electrolyte side 33 to the air side 34. The weight percent ratio of (active hydrophilic material):(active hydrophobic material) in the active layer 17 is about (30% to 50%):(50% to 70%), usually about 40%:60%. The weight ratio of (active hydrophilic material):(active hydrophobic material) through the thickness of the active layer 17 can range from about (1):(0.2) at the electrolyte contact side 33 to about (1):(5) at the air contact side, i.e., the porous backing sheet contact side.

For example, active material section A may contain 1.5 parts of hydrophilic material having a particle size of about 800 μm and 0.5 part of hydrophobic material having a particle size of about 650 μm . Section B may contain 1.5 parts of hydrophilic material having a particle size of about 800 μm and 1.5 parts of hydrophobic material having a particle size of about 650 μm . Section C may contain 1.0 part of hydrophilic material having a particle size of about 1,000 microns and 2.0 parts of hydrophobic material having a particle size of about 700 μm . Section D may contain 0.5 part of hydrophilic material having a particle size of about 1,100 μm and 2.5 parts of hydrophobic material having a particle size of about 1,100 μm . Thus, the particle size of hydrophilic material increases from side 33 to side 34, i.e., from 800 to 1,100 μm , and the particle size of hydrophobic material also increases from side 33 to side 34, i.e., from 650 to 1,100 μm ; and the weight ratio of (hydrophilic material):(hydrophobic material) increased from side 33 to side 34, i.e., from (1):(0.3) to (1):(5).

It is critical to the invention that the active layer be electrochemically active throughout, that the active material comprise both hydrophilic material and hydrophobic material in a homogenous admixed combination in each active section, and that there be both an agglomerate particle size gradient and a weight ratio gradient from the electrolyte contact side to the air contact side through the active layer of the electrode structure. This concept dramatically reduces electrolyte flooding problems after extended cycling, providing an almost ideal three phase interface between electrolyte, air or oxygen, and catalyst contained throughout the active material. The term "hydrophilic material" means agglomerates through which electrolyte can readily permeate and flow. The term "hydrophobic material" means agglomerates which tend to retain electrolyte or prevent its flow, yet which easily pass air. Importantly, catalyst is equally distributed throughout the active layer, even in section D, next to the porous backing layer 14, and bonding/nonwetting material is equally distributed throughout the active layer, even in section A next to the electrolyte contact surface 33, as described hereinafter.

The catalytically active material, 30 in Fig. 2, contained in each active material section A, B, C, and D, comprises: an oxygen absorption/reduction carbon, preferably having a BET total surface area of from about 30 square meters per gram to about 300 square meters per gram; a suitable catalyst, such as silver preferably coated or otherwise contained on or in the carbon particles; preferably, a low oxygen overvoltage metal additive such as CoWO_4 , WS_2 , nickel spinels, and preferably NiS , FeWO_4 , WC , WC coated with 1 to 20 weight percent Co, and their mixtures; and a fluorocarbon particle dispersion, preferably a polytetrafluoroethylene dispersion, as a bonding/nonwetting material, where the dispersion agent is a heat vaporizable or decomposable organic material that is effective to reduce surface tension between the fluorocarbon and other particles and promote electrolyte capillary flow between particles in the active material. Useful dispersion agents include anionic surfactants, such as sodium alkaryl polyether sulfonate, sodium alkaryl polyether sulfate, sodium alkaryl ether sulfate, dioctyl sodium sulfosuccinate, and phosphate esters in acid form, and the like, and their mixtures; and preferably non-ionic surfactants, such as octyl phenol ether alcohol, octyl phenol polyether alcohol, nonyl phenol polyether alcohol, alkylpolyether alcohol, alkylaryl polyethylene glycol ether, and the like, and their mixtures, and mixtures with anionic surfactants, as are well known in the art. Cationic surfactants, having a negative charge, tend to repel electrolyte penetration and are not particularly useful.

The useful carbon in this invention is preferably in a fluffy form comprising discrete particles in a chain-like form, such as acetylene black. If in a pressed pellet form, it can be ground to a useful particle size. Acetylene black has a low resistivity of from 0.035 to 0.22 ohms/cubic inch (2.13×10^{-3} to 1.3×10^{-2} ohm/ cm^3) at 2,500 psi (17218 kPa), making it an excellent electron conductor. It has a bulk density of about 1.20 lb./cubic foot (0.01928 g/ cm^3), a particle size of from 0.005 to 0.13 μm , and each particle contains few pore openings greater than 0.002 μm on its external surface. Almost all of its surface area is external, there being few internal channels. Certain channel carbon black materials are also useful. The preferred BET total surface area range for the carbon is from 30 to 300 square meters per gram.

As a bifunctional air electrode in a metal-air battery, the carbon acts as a surface to evolve oxygen during electrode charging. The carbon also usually serves as a surface for the silver, nickel, platinum or other suitable catalyst, depending on electrode application, which can be applied to the carbon. In one method of applying silver, the preferred catalyst for metal-air battery applications, carbon is mixed with AgNO_3 solution and the silver precipitated out and onto the carbon with hydrazine. A further more complete description of various carbons, the BET (Brunauer, Emmett and Teller) method of measuring surface area, and various low oxygen overvoltage metal additives, can be found in U.S. Patent Specification No. 3,977,901.

Very importantly, after admixing all the component ingredients, all of the hereinbefore described catalytically active material is air dried at from 25°C to 30°C for 12 to 48 hours, providing an active all hydrophilic material. Then a portion of this hydrophilic material is heat treated by oven baking at from 250°C to 325°C for about 1 to 3 hours in air or a flowing gas atmosphere. This heat treatment causes the dispersion agent for the fluorocarbon to thermally decompose or vaporize to provide a hydrophobic material which will retain electrolyte because the dispersion agent, usually a surfactant, is not present to reduce surface tension and allow good capillary flow of the electrolyte.

The air dried portion and the heat treated portion are size graded to provide agglomerates or particle masses ranging from 150 μm to 2,000 μm , for metal-air battery applications, and from 30 microns to 300 microns for fuel cell applications. They are then admixed in the appropriate amounts to provide the weight

range gradient described hereinbefore. By the term "agglomerates" is meant a combined mass comprising a plurality of the extremely fine carbon particles together with the coarser fluorocarbon and the metal additive particles which are particularly useful in metal-air battery applications. These range in particle size from 0.5 to 50 μm for the former, and 50 to 200 μm for the latter.

5 For both the hydrophilic and hydrophobic materials, the amount of fluorocarbon bonding/nonwetting solids may vary from about 10 weight percent to about 50 weight percent of the total composition. Usually the fluorocarbon dispersion contains from 50% to 60% fluorocarbon solids, and 5% to 10% dispersing agent, with the rest of the dispersion as water. Low oxygen overvoltage material can be added in the amount of from 0.25 part to 5 parts/part carbon. These materials may act as pore formers and in some
10 instances prevent catalyst dissolution. The carbon will generally contain from 2 weight percent to 10 weight percent, preferably from 2 to 5 weight percent silver or other suitable catalyst.

These electrodes are particularly useful in electrochemical energy cells, which can be combined to form metal/air batteries, where the metal electrode can be iron, zinc, cadmium, or aluminum with alkali hydroxide electrolyte disposed between and contacting the electrodes.

15 These electrodes can also find use as electrodes in a variety of fuel cells, such as room temperature alkaline fuel cells and high temperature phosphoric acid fuel cells, both of which are well known in the art. There, a fuel electrode contacts a fuel, such as hydrogen gas and an air electrode contacts air or oxygen, and electrolyte contacts the fuel electrode and the air electrode. In such applications, the electrode of this invention can be used as either the fuel electrode or the air electrode, and the electrolyte, such as
20 potassium hydroxide or phosphoric acid, is disposed between the fuel and air electrodes. Reference may be made to U.S. Patent 3,935,029, herein incorporated by reference, for a complete description of fuel cell operation and standard electrode construction.

The invention will now be illustrated with reference to the following Example:

Example

25 A 4.5 inch \times 4.5 inch (11.43 \times 11.43 cm) air electrode was made. Dry acetylene carbon black particles, having a BET surface area of from about 60 to 70 square meters per gram (sold commercially by Shawinigan Products Corp. under the tradename Shawinigan Black) were mixed with AgNO_3 in a wet slurry. Hydrazine was then added to precipitate the silver on the carbon particles. Excess water was then
30 vacuumed off and the paste allowed to air dry for 24 hours. Sufficient AgNO_3 solution was used to provide a 3 to 4 weight percent silver content on the surface of the carbon particles. To 30 grams of this silverized carbon powder was added 4.5 grams of NiS ; 4.5 grams of FeWO_4 ; 4.5 grams of WC coated with 12 weight percent Co; 12 grams of aqueous polytetrafluoroethylene dispersion containing 7.2 grams of
35 polytetraethylene solids and about 1.0 gram of an octylphenol polyether alcohol non-ionic surfactant dispersing agent, and 170 ml. of water, to form a slurry. The slurry was then air dried on a screen at 25°C for 24 hours to provide an active hydrophilic material.

The mixture of low oxygen overvoltage materials was present in an amount of about 0.45 part/part carbon, and the polytetraethylene solids constituted about 14 weight percent of the air dried, catalyzed material. About 60 weight percent of the air dried, catalyzed material was placed in an oven and baked at
40 300°C for 2 hours, to vaporize and decompose the nonionic surfactant and provide a heat treated active hydrophobic material. Without the surfactant, this material would provide little capillary penetration of electrolyte. Both the active hydrophilic material and the active hydrophobic material had the same amount of catalyst and polytetrafluoroethylene present, and both were sieved and size graded to provide batches of hydrophilic agglomerates having particle sizes of 793 microns and 1,098 μm , and batches of hydrophobic
45 agglomerates having particle sizes of 660 microns, 793 μm and 1,098 μm .

Four 4.5 inch \times 4.5 inch \times 0.01 inch thick (11.43 \times 11.43 \times 0.025 cm) diffusion bonded, 94% porous, nickel fiber wool plaques were used as the current collectors, to provide an air electrode structure similar to that shown in Fig. 2 of the drawings. All plaques were welded along their upper edge to an electrical lead tab. The catalytically active material sections were laid down as follows, where HL=active hydrophilic material
50 and HP=active hydrophobic material.

A—next to electrolyte:

1.2 g. HL at 793 micron+
0.8 g. HP at 660 micron
Nickel Fiber Plaque

55 B—next to A:

1.2 g. HL at 793 micron+
1.8 g. HP at 660 micron
Nickel Fiber Plaque

C—next to D:

1.0 g. HL at 1,098 micron+
1.5 g. HP at 660 micron+
0.5 g. HP at 793 micron
Nickel Fiber Plaque

60 D—next to air contact:

0.8 g. HL at 1,098 micron+
0.5 g. HP at 1,098 micron+
1.7 g. HP at 793 micron
Nickel Fiber Plaque

Each section of catalyzed active material was cold pressed into its corresponding nickel plaque at 2,500 lb./sq. inch, to provide a coating on and at least partial impregnation of the corresponding plaque.

At this point a hydrophobic sheet was made by mixing carbon black particles and polytetrafluoroethylene in a mill, to fibrillate the polytetrafluoroethylene, and then cold pressing the milled admixture at 2,500 lb./sq. inch (1.72×10^4 kPa) into a sheet form. The hydrophobic sheet was then placed on the platen of a hot bed press and sections D, C, B and A respectively superimposed thereon to provide an electrode stack up. The entire stack up was then heat and pressure consolidated in the hot bed press at 4,000 lb./sq. inch (2.75×10^4 kPa) and 300°C, to provide a unitary air electrode similar in structure to that shown in Fig. 2.

The active layer of the air electrode consisted of 38 weight% hydrophilic material and 62 weight% hydrophobic material excluding plaque weight, and the weight ratio of active hydrophilic material:active hydrophobic material ranged from 1.2:0.8 or 1:0.67 for the section next to electrolyte, to 0.8:(0.5+1.7) or 1:2.5 for the section next to the hydrophobic sheet on the air side. Also, the particle size of the hydrophilic material increased from 793 to 1,098 μ m and the particle size of the hydrophobic material increased from 660 to 1,098 microns from the electrolyte to the air side.

The consolidated air electrode, containing 4 active material sections and 4 current collectors was used as one side of a square plastic container filled with a 25 wt.% KOH electrolyte solution, where the hydrophobic sheet contacted an air source and section A of the air electrode contacted the electrolyte. The plastic framed the air electrode, similarly as shown in Fig. 1 of the drawings, so that the active surface was reduced to about 3-1/4 inch \times 3-3/4 inch (8.25 \times 9.52 cm). A flat nickel sheet formed the opposite wall of the cell acting as a counter electrode. A polytetrafluoroethylene sheet was used to cover the side of the nickel counter electrode not in contact with electrolyte. A Hg/HgO reference electrode was inserted into the electrolyte between the nickel sheet and the air electrode, and suitable electrical connections were made. This electrical cell, using the air electrode of this invention, was then cycled for 250 cycles, where 1 cycle=4 hours discharge at 25 mA/sq. cm.+4 hours charge at 12.5 mA/sq. cm.

A graph of oxygen reduction potential vs. cycle, Fig. 3, and oxygen evolution potential vs. cycle, Fig. 4, was made, where curve A in each graph represents the cell performance using the air electrode of this invention. As can be seen, the air electrode of this invention, having both a size and weight grading across its active layer, exhibited stable electrical characteristics, with no major potential changes, indicating no uncontrolled electrolyte flooding of any active regions and no structural delaminations in any active regions due to oxygen entrapment. Testing was continued and the curve remained stable up to 300 cycles. Such dramatic results indicate the superiority of the air electrode of this invention, and indicate its usefulness in a non-flooding metal-air battery. A comparative material represented by curve B in each graph is described below.

For purposes of comparison, a 4.5 inch \times 4.5 inch (11.43 \times 11.43 cm) air electrode was made utilizing four 4.5 inch \times 4.5 inch \times 0.01 inch (11.43 \times 11.43 \times 0.025 cm) thick diffusion bonded, 94% porous, nickel fiber wool plaques as current collectors. The ingredients and amounts for the active material were the same as used in Example 1, so that the mixture of low oxygen overvoltage materials was present in an amount of about 0.45 part/part carbon, and the polytetraethylene solids constituted about 14 weight percent of the air dried, catalyzed material. A small percent of the air dried, catalyzed material was baked, as described in Example 1, to provide a hydrophobic material. Both the active hydrophilic material and the active hydrophobic material had the same amount of catalyst and polytetrafluoroethylene present, and both were sieved and size graded to provide hydrophilic and hydrophobic agglomerates, both having particle sizes of approximately 2,500 μ m.

The catalytically active material sections were laid down as follows, where HL=active hydrophilic material and HP=active hydrophobic material:

50	A—next to electrolyte:	1.5 g. HL at approximately 2,500 μ m Nickel Fiber Plaque
	B—next to A:	1.5 g. HL at approximately 2,500 μ m Nickel Fiber Plaque
	C—next to D:	1.5 g. HL at approximately 2,500 μ m Nickel Fiber Plaque
60	D—next to air contact:	1.5 g. HL at approximately 2,500 μ m+ 0.4 g. HP at approximately 2,500 μ m Nickel Fiber Plaque

Thus, unlike Example 1, there was neither a homogeneous mixture of hydrophilic and hydrophobic agglomerates through the active layer, nor a particle or weight gradient through the active layer.

As in Example 1, each section of catalyzed active material was cold pressed into its corresponding nickel plaque, and a stack up prepared and hot bed pressed to a hydrophobic sheet to provide a unitary air electrode containing 4 active material sections and 4 current collectors. This comparative air electrode was

then used as the air electrode of an electrical cell, as described in Example 1 and then cycled for 250 cycles, where 1 cycle=4 hours discharge at 25 mA/sq. cm.+4 hours charge at 12.5 mA/sq. cm.

A graph of oxygen reduction potential and oxygen evolution potential vs. cycle was made, Fig. 3 and Fig. 4 respectively, where curve B in each graph represents the cell performance using this comparative air electrode. As can be seen, curve B in both graphs shows major potential changes and a lack of stability through the 250 cycles.

As described hereinabove, the size and weight graded, multi-ply laminar electrodes of this invention can also be used in fuel cell applications.

10 Claims

1. An electrode for use in electrochemical energy cells which comprises: a porous backing sheet and a catalytically active layer comprising catalyst and a mixture of hydrophobic agglomerates and hydrophilic agglomerates, said layer being attached to said porous backing sheet having an electrolyte permeable side and a backing sheet contacting side, characterized in that the particle size of the hydrophobic agglomerates and the hydrophilic agglomerates increases from the electrolyte permeable side to the backing sheet contacting side and the weight ratio of hydrophobic material:hydrophilic material increases from the electrolyte permeable side to the backing sheet contacting side.

2. An electrode according to claim 1, characterized in that the hydrophobic agglomerates comprises carbon particles and fluorocarbon material; the hydrophilic agglomerates comprise carbon particles, fluorocarbon material and an organic dispersion agent effective to reduce liquid surface tension between the hydrophilic agglomerates; and the catalyst is disposed equally throughout the active layer.

3. An electrode according to claim 1 or 2, characterized in that said electrode is an air electrode in which the backing sheet is hydrophobic to which is laminated the catalytically active layer which has at least two porous metallic current collectors disposed therein; said hydrophobic agglomerates comprising oxygen absorption/reduction carbon particles having a total surface area of from 30 to 300 square meters per gram; catalyst, low oxygen overvoltage material, and fluorocarbon bonding/nonwetting material; and said active hydrophilic agglomerates comprising oxygen absorption/reduction carbon particles having a total surface area of from 30 to 300 square meters per gram, catalyst, low oxygen overvoltage material; fluorocarbon bonding/non-wetting material, and an organic dispersion agent effective to reduce liquid surface tension between the hydrophilic agglomerates; the weight ratio of active hydrophilic material:active hydrophobic material varying from 1:0.2 at the highly electrolyte permeable side to 1:5 at the hydrophobic sheet contacting side.

4. An electrode according to claim 3, characterized in that the current collectors in the active layer comprise a metal fiber structure, the catalyst in the active layer is effective for the decomposition of perhydroxides, and the low oxygen overvoltage material in the active layer is CoWO_4 , WS_2 , nickel spinels, NiS , FeWO_4 , WC , WC coated with 1 wt.% to 20 wt.% Co, or mixtures thereof.

5. An electrode according to claim 3 or 4, characterized in that the fluorocarbon in the active layer is polytetrafluoroethylene and the catalyst in the active layer is silver, said silver being deposited on the carbon particles.

6. An electrode of claim 3, 4 or 5, characterized in that the organic dispersion agent is an anionic surfactant, a non-ionic surfactant, or mixtures thereof.

7. An electrode according to claim 6, characterized in that the organic dispersion agent is octyl phenol ether alcohol, octyl phenol polyether alcohol, nonyl phenol polyether alcohol, alkylpolyether alcohol, alkylaryl polyethylene glycol ether or mixtures thereof.

8. An electrode according to any of claims 3 to 7, characterized in that the agglomerates in the active layer have a particle size diameter ranging from 150 microns to 2,000 microns.

9. An electrode according to any of claims 3 to 8, characterized in that the active layer is made up of at least two active material sections with a current collector between adjacent sections and between said backing sheet and said section adjacent thereto.

10. A metal/air cell, characterized in that said cell comprises a metal electrode, at least one air electrode as claimed in any of claims 3 to 9 and spaced apart from said metal electrode, and an alkali hydroxide electrolyte in contact with said metal and air electrode.

11. A cell according to claim 10, characterized in that the metal electrode is of iron, zinc, cadmium or aluminum.

12. A fuel cell characterized in that said cell comprises a fuel electrode, an electrode as claimed in claim 1 or 2 and spaced apart from said fuel electrode, and an electrolyte in contact with said electrodes.

Patentansprüche

1. Eine Elektrode zur Verwendung in elektrochemischen Energiezellen, die folgendes umfaßt: Eine poröse Rückenschicht und eine katalytisch aktive Schicht, die einen Katalysator und eine Mischung von hydrophoben Agglomeraten und hydrophilen Agglomeraten umfaßt, wobei die Schicht, angebracht an der porösen Rückenschicht, eine elektrolitisch permeable Seite und die eine Rückenschicht berührende Seite aufweist, dadurch gekennzeichnet, daß die Teilchengröße der hydrophoben Agglomerate und der

hydrophilen Agglomerate von der elektrolytisch permeablen Seite zur die Rückenschicht berührenden Seite ansteigt und das Gewichtsverhältnis hydrophobes Material:hydrophiles Material von der elektrolytisch permeablen Seite zur die Rückenschicht berührenden Seite anwächst.

2. Eine Elektrode nach Anspruch 1, dadurch gekennzeichnet, daß die hydrophoben Agglomerate Kohlenstoffteilchen und Fluorokohlenstoffmaterial umfassen; daß die hydrophilen Agglomerate Kohlenstoffteilchen, Fluorokohlenstoffmaterial und ein organisches Dispersionsmittel, wirksam zur Reduktion von Flüssigkeitsoberflächenspannung zwischen den hydrophilen Agglomeraten, umfaßt; und daß der Katalysator gleichförmig in der aktiven Schicht verteilt ist.

3. Eine Elektrode nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Elektrode eine Lufterlektrode ist, in der die Rückenschicht hydrophob ist, auf welche die katalytisch aktive Schicht auf laminiert ist, die zumindest zwei poröse metallische Stromkollektoren darin angeordnet besitzt; wobei die hydrophoben Agglomerate sauerstoffabsorbierende/reduzierende Kohlenstoffteilchen, die ein gesamtes Oberflächengebiet von 30 bis 300 m² pro Gramm aufweisen; Katalysator, Niedrig-Sauerstoff-Überspannungsmaterial und Fluorokohlenstoff bindendes/nicht-benetzendes Material umfassen; und daß die aktiven hydrophilen Agglomerate sauerstoffabsorbierende/reduzierende Kohlenstoffteilchen mit einem Gesamtoberflächengebiet von 30 bis 300 m² pro Gramm, Katalysator, Niedrig-Sauerstoff-Überspannungsmaterial; Fluorokohlenstoff bindendes/nichtbenetzendes Material, und ein organisches Dispersionsmittel, wirksam zur Reduzierung der Flüssigkeitsoberflächenspannung zwischen den hydrophilen Agglomeraten, umfassen; wobei das Gewichtsverhältnis von aktives hydrophiles Material: aktives hydrophobes Material von 1:0,2 an der stark Elektrolyt durchlassenden Seite bis 1:5 an der die hydrophobe Schicht berührenden Seite variiert.

4. Eine Elektrode nach Anspruch 3, dadurch gekennzeichnet, daß die Stromkollektoren in der aktiven Schicht eine Metallfaserstruktur umfassen, der Katalysator in der aktiven Schicht wirksam ist zur Zersetzung der Perhydroxide, und das Niedrig-Sauerstoff-Überspannungsmaterial in der aktiven Schicht CoWO₄, WS₂, Nickel-Spinell, NiS, FeWO₄, WC, mit 1 bis 20 Gew.-% Co beschichtetes WC, oder Mischungen davon ist.

5. Eine Elektrode nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß der Fluorokohlenstoff in der aktiven Schicht Polytetrafluoroäthylen und der Katalysator in der aktiven Schicht Silber ist, wobei das Silber auf den Kohlenstoffteilchen abgelagert ist.

6. Eine Elektrode nach Anspruch 3, 4 oder 5, dadurch gekennzeichnet, daß das organische Dispersionsmittel ein anionisches Netzmittel, ein nicht-ionisches Netzmittel oder Mischungen davon ist.

7. Eine Elektrode nach Anspruch 6, dadurch gekennzeichnet, daß das organische Dispersionsmittel Octyl-Phenol-Äther-Alkohol, Octyl-Phenol-Polyäther-Alkohol, Nonyl-Phenol-Polyäther-Alkohol, Alkylpolyäther-Alkohol, Alkylaryl-Polyäthylen-Glykol-Äther oder Mischungen davon ist.

8. Eine Elektrode nach einem der Ansprüche 3 bis 7, dadurch gekennzeichnet, daß die Agglomerate in der aktiven Schicht einen Teilchengrößendurchmesser besitzen, der von 150 Mikron bis 2.000 Mikron reicht.

9. Eine Elektrode nach einem der Ansprüche 3 bis 9, dadurch gekennzeichnet, daß die aktive Schicht aus zumindest zwei aktiven Materialabschnitten hergestellt ist, mit einem Stromkollektor zwischen angrenzenden Abschnitten und zwischen der Rückenschicht und dem dazu angrenzenden Abschnitt.

10. Eine Metall-Luft-Zelle, dadurch gekennzeichnet, daß die Zelle eine Metallelektrode, zumindest eine Lufterlektrode nach einem der Ansprüche 3 bis 9, angeordnet im Abstand von der Metallelektrode, und einen Alkali-Hydroxid-Elektrolyten in Kontakt mit der Metall- und der Lufterlektrode umfaßt.

11. Eine Zelle nach Anspruch 10, dadurch gekennzeichnet, daß die Metallelektrode aus Eisen, Zink, Kadmium oder Aluminium ist.

12. Eine Brennstoff-Zelle, dadurch gekennzeichnet, daß die Zelle eine Brennstoffelektrode, eine Elektrode nach einem der Ansprüche 1 oder 2 und im Abstand von der Brennstoffelektrode angeordnet, sowie einen Elektrolyten in Kontakt mit den Elektroden aufweist.

50 Revendications

1. Electrode destinée à être utilisée dans des piles d'énergie électrochimique, comprenant: une feuille de support poreuse et une couche à activité catalytique comprenant un catalyseur et un mélange d'agglomérés hydrophobes et d'agglomérés hydrophiles, cette couche fixée à la feuille de support poreuse présentant un côté perméable à l'électrolyte et un côté venant en contact avec la feuille de support, électrode caractérisée en ce que la taille de particules des agglomérés hydrophobes et des agglomérés hydrophiles, augmente lorsqu'on passe du côté perméable à l'électrolyte au côté en contact avec la feuille de support, et en ce que le rapport de poids entre le matériau hydrophobe et le matériau hydrophile, augmente lorsqu'on passe du côté perméable à l'électrolyte au côté en contact avec la feuille de support.

2. Electrode selon la revendication 1, caractérisée en ce que les agglomérés hydrophobes sont constitués par des particules de carbone et un matériau de fluorure de carbone; en ce que les agglomérés hydrophiles sont constitués par des particules de carbone, un matériau de fluorure de carbone et un agent de dispersion organique destiné à réduire la tension de surface du liquide entre les agglomérés hydrophiles; et en ce que le catalyseur est également réparti dans toute la couche active.

3. Electrode selon l'une quelconque des revendications 1 et 2, caractérisée en ce que l'électrode est une

électrode d'air dans laquelle la feuille de support est une feuille hydrophobe sur laquelle est stratifiée la couche à activité catalytique dans laquelle sont disposés au moins deux collecteurs de courant métalliques poreux; en ce que les agglomérés hydrophobes comprennent des particules de carbone d'absorption/réduction d'oxygène présentant une surface totale comprise entre 30 et 300 m² par gramme, un catalyseur, un matériau à faible surtension d'oxygène, et un matériau agglomérant/non mouillant de fluorure de carbone; en ce que les agglomérés hydrophiles actifs comprennent des particules de carbone d'absorption/réduction d'oxygène présentant une surface totale comprise entre 30 et 300 m² par gramme, un catalyseur, un matériau à faible surtension d'oxygène, un matériau agglomérant/non mouillant de fluorure de carbone, et un agent de dispersion organique servant à réduire la tension de surface du liquide entre les agglomérés hydrophiles; et en ce que le rapport de poids entre le matériau hydrophile actif et le matériau hydrophobe actif varie de 1:0,2 du côté fortement perméable à l'électrolyte, à 1:5 du côté en contact avec la feuille hydrophobe.

4. Electrode selon la revendication 3, caractérisée en ce que les collecteurs de courant de la couche active sont constitués par une structure de fibres métalliques, en ce que le catalyseur de la couche active sert à décomposer des perhydroxydes et en ce que le matériau à faible surtension d'oxygène de la couche active est constitué par du CoWO₄, du VS₂, des spinelles de nickel, du NiS, du FeWO₄, du WC, du WC revêtu de 1% à 20% en poids de Co, ou des mélanges de ces produits.

5. Electrode selon l'une quelconque des revendications 3 et 4, caractérisée en ce que le fluorure de carbone de la couche active est du polytétrafluoréthylène, et en ce que le catalyseur de la couche active est de l'argent, cet argent étant déposé sur les particules de carbone.

6. Electrode selon l'une quelconque des revendications 3 à 5, caractérisée en ce que l'agent de dispersion organique est un surfactant anionique, un surfactant non anionique, ou un mélange de ceux-ci.

7. Electrode selon la revendication 6, caractérisée en ce que l'agent de dispersion organique est de l'alcool éther phénol octyl, de l'alcool polyéther phénol octyl, de l'alcool polyéther phénol nonyl, de l'alcool alkylpolyéther, de l'éther glycolpolyéthylène alkylaryl, ou des mélanges de ces produits.

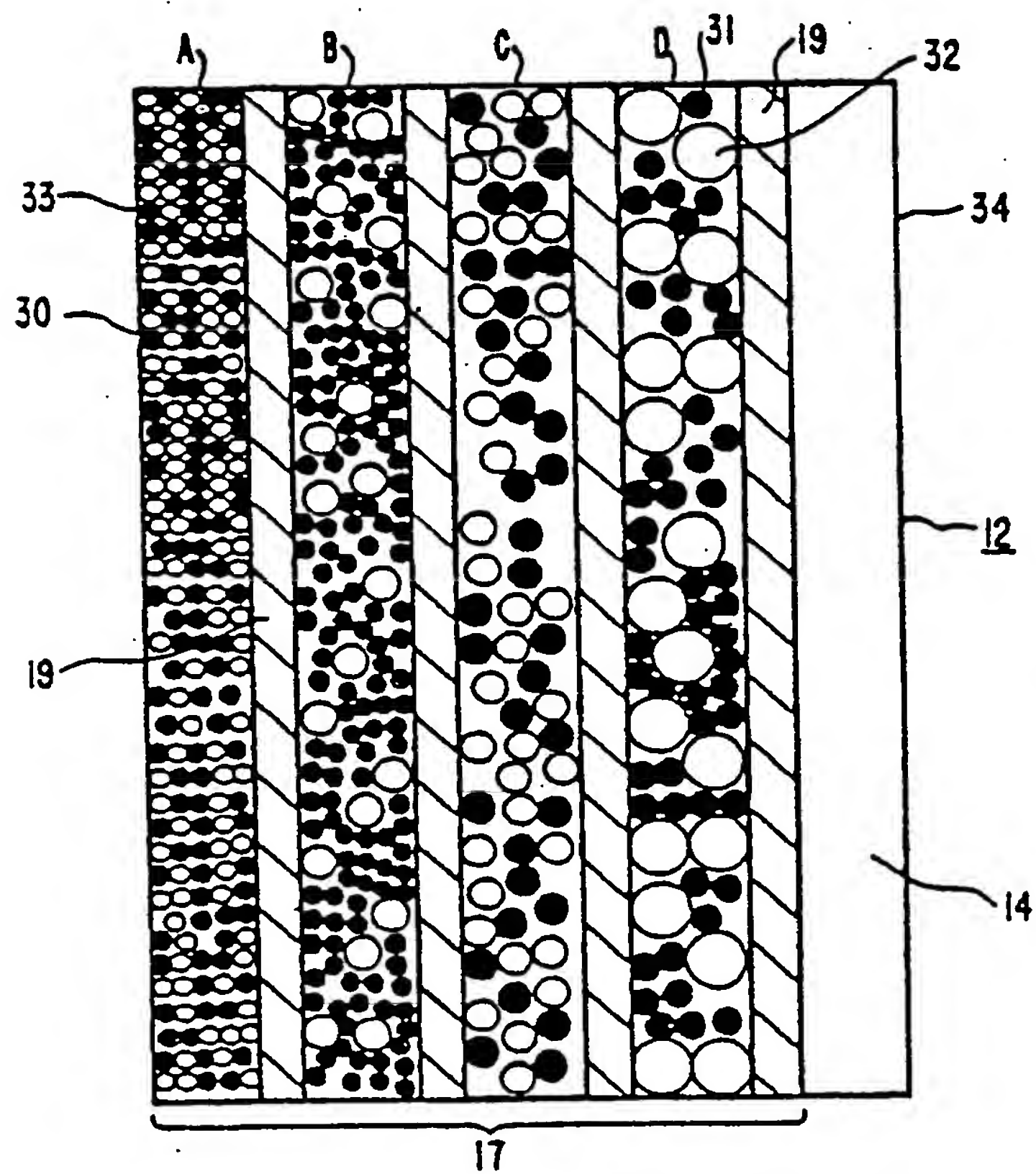
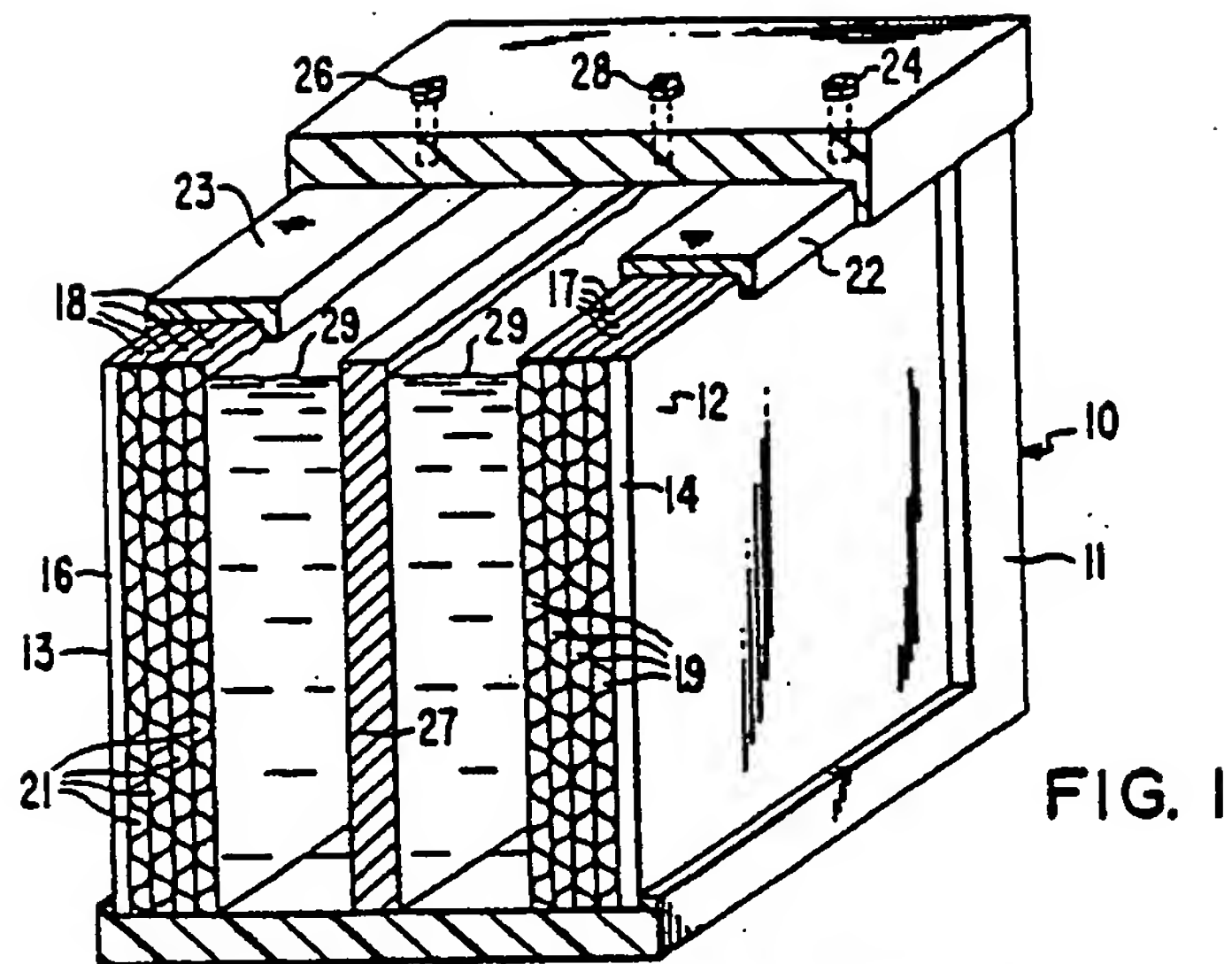
8. Electrode selon l'une quelconque des revendications 3 à 7, caractérisée en ce que les agglomérés de la couche active présentent un diamètre de particules se situant entre 150 µm et 2000 µm.

9. Electrode selon l'une quelconque des revendications 3 à 8, caractérisée en ce que la couche active est constituée d'au moins deux sections de matériau actif, avec un collecteur de courant placé entre sections adjacentes et entre la feuille de support et la section adjacente à celle-ci.

10. Pile à métal/air, caractérisée en ce que cette pile comprend une électrode métallique, au moins une électrode d'air, telle que celle revendiquée dans l'une quelconque des revendications 3 à 9 et placée à une certaine distance de l'électrode métallique, et un électrolyte en hydroxyde alcalin venant en contact avec l'électrode métallique et l'électrode d'air.

11. Pile selon la revendication 10, caractérisée en ce que l'électrode métallique est en fer, en zinc, en cadmium ou en aluminium.

12. Pile à combustible caractérisée en ce que cette pile comprend une électrode de combustible, une électrode telle que celle revendiquée dans l'une quelconque des revendications 1 et 2, celle-ci étant espacée de l'électrode de combustible, et un électrolyte venant en contact avec ces électrodes.



0 110 491

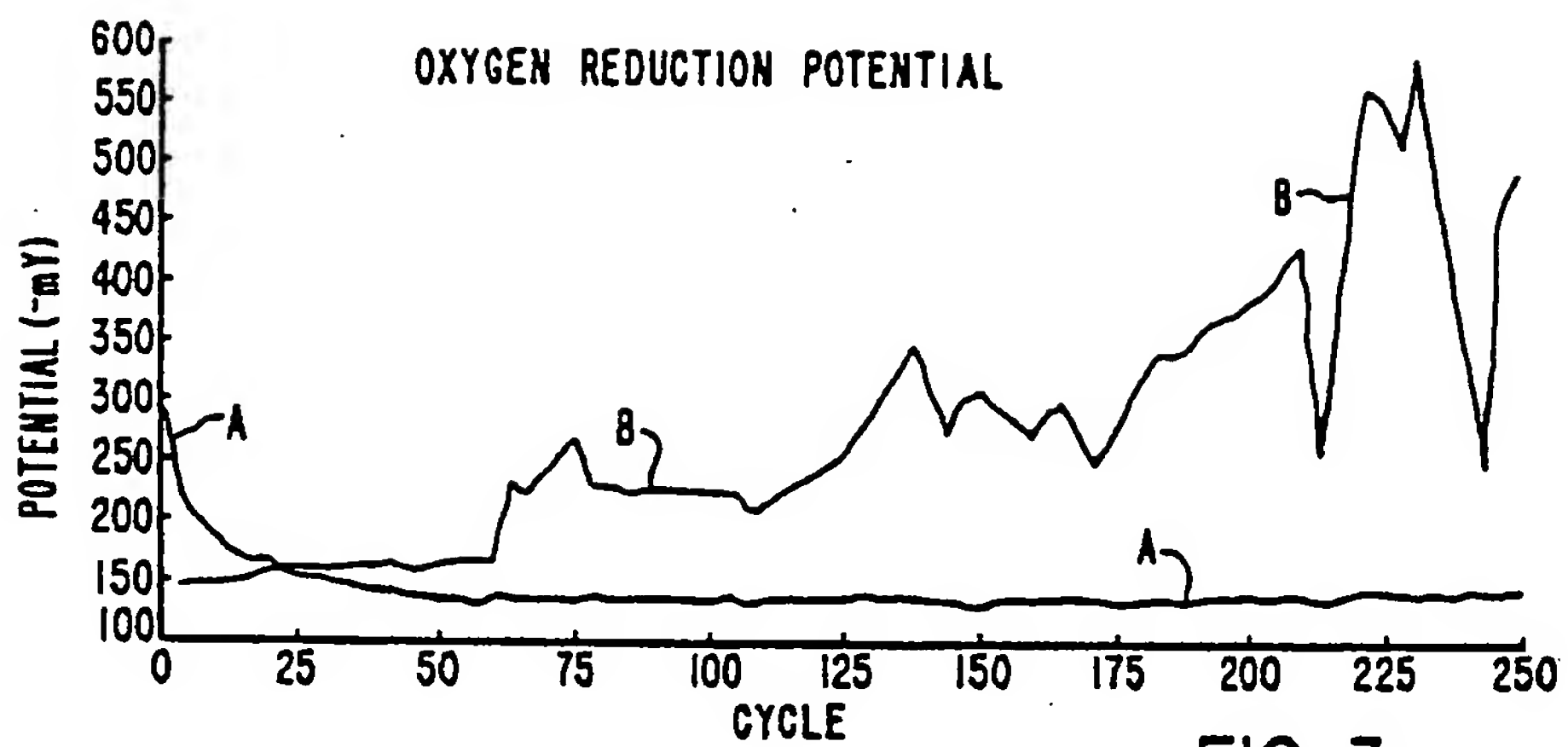


FIG. 3

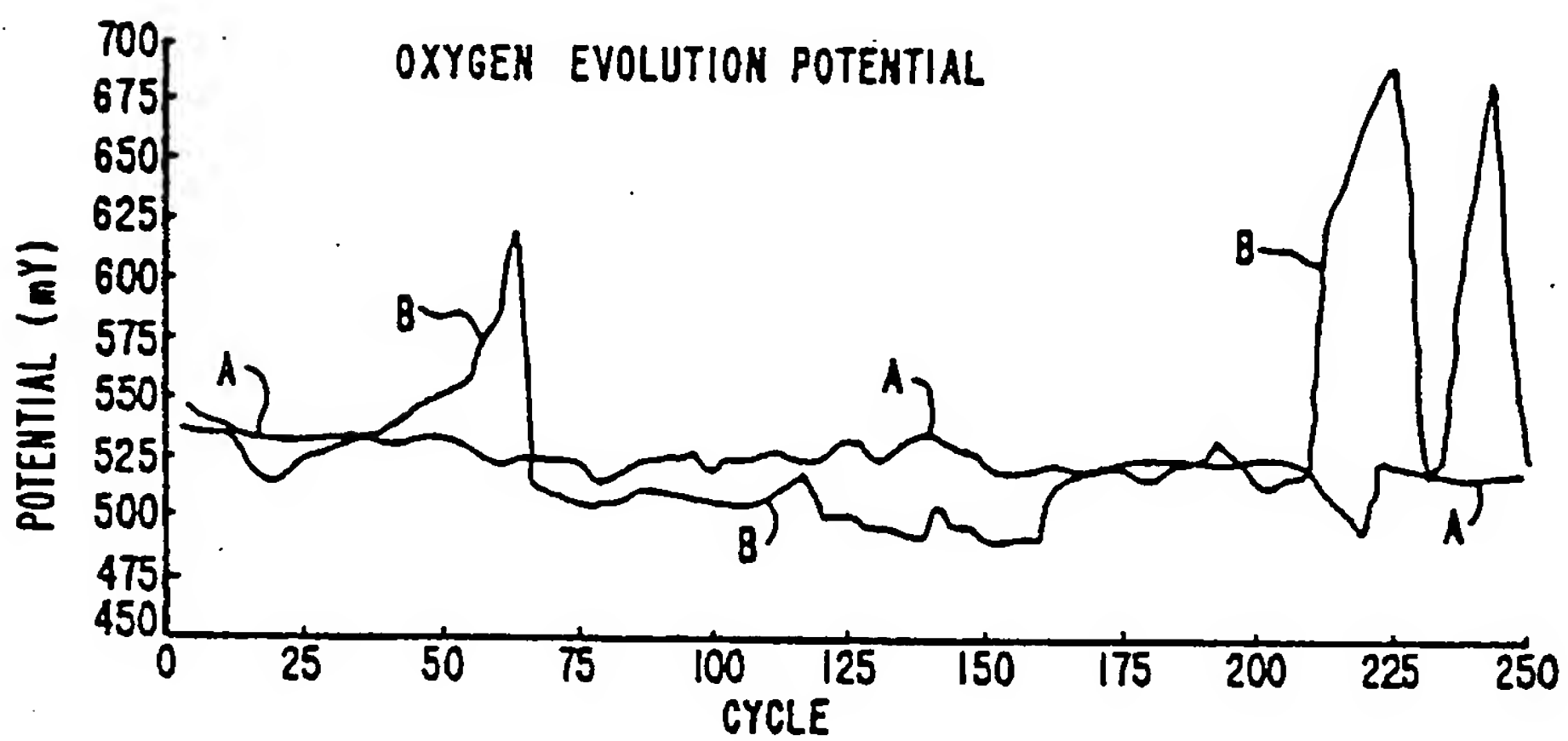


FIG. 4